Encl. 1 (P. 1/3)
JP 01-108972

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審査請求　未請求　発明の数 1　（全7頁）

⑭発明の名称　液－液異相系の反応装置

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㉒出　願　昭62(1987)10月21日

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第 89125938 號
初審（訴願）證附件
再審

明細書

1. 発明の名称

液－液異相系の反応装置

2. 特許請求の範囲

1 孔を有する仕切板により上下に2以上の隔室に仕切られており、各隔室にはそれぞれ内外に仕切る中壁が設けられると共に、内室側に撹拌翼が取付けられており、最上層の隔室にはその上部に重液相導入口および軽液相の抜取口が設けられており、最下層の隔室には撹拌翼の下方に、軽液相導入口が設けられ、最下層の隔室に重液相出口が設けられてなる互いに不溶あるいは難溶で比重の異なる2液相の液－液異相系の反応装置。

3. 発明の詳細な説明

（産業上の利用分野）

本発明は液－液異相反応系において、これら異相を撹拌混和しながら連続多段反応を行い、しかも反応と同時に同じ反応器内でこれら異相を連続的に分離し効率よく生成物を得る反応装置に関するものである。

〔従来の技術およびその問題点〕

化学工業における化学反応はその大部分が異相系（気－液、気－固、液－固、液－液、固－固）での反応であり、その中の一つである液－液異相反応においても有用な反応は数多くある。例えば、リパーゼによる油脂の加水分解、油脂の改質、油脂の合成や種々のエステルの合成反応、またプロテアーゼを利用した人工甘味料アスパルテームの合成等にみられる種々のペプチド合成反応、あるいは有機化合物のニトロ化反応、スルホン化反応やアルキル化反応等が挙げられる。これら異相系反応は一般には、反応効率を高めるため、通常、微細なエマルションとして反応を行い、所定反応率に達した後、反応を停止して、次にそれぞれの相に分離して生成物を回収する回分操作となる。また、原料物質を連続的に供給し、連続反応を行うことも可能であるが、この場合反応器の後にエマルションを分離する工程がさらに必要となる。

Encl. 1 (P.2/3)
JP 59-196733

⑲ 日本国特許庁 (JP)　　⑪ 特許出願公開

⑫ 公開特許公報 (A)　　昭59—196733

⑤Int. Cl.³　B 01 J 19/00　識別記号　庁内整理番号 Z 6542—4G

④公開 昭和59年(1984)11月8日

発明の数 1
審査請求 未請求

(全 5 頁)

⑤反応装置

②特　　願 昭58—70071
②出　　願 昭58(1983)4月22日

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第 89125938 號
初審 ~~再審~~ (~~訴願~~) 引證附件

明細書

1.発明の名称

反応装置

2.特許請求の範囲

一端に反応に供する液体入口をまた他端に反応生成物の流出口を設けた撹拌翼付き反応容器において、該反応容器の内壁面上に付設された仕切り効果を有する静止部分域板によって該容器が複数のセルに分割されており各々のセルは同一の撹拌軸を共有して撹拌翼を備えていることを特徴とする気－液又は液－液反応装置。

3.発明の詳細な説明

本発明は気－液又は液－液反応装置にかんし、とくに重合体の連続的改質反応装置にかんする。

気－液反応系においては溶媒に溶解した状態の重合体と気体状の改質剤とを接合接触させて反応を行なわせ、液－液反応系では溶媒に溶解した状態の重合体と該重合体溶液よりも粘性の小さい液体状の改質剤とを接合接触させて反応を行なわせる。かかる気－液又は液－液反応系では均一で高い反応率を達成するためには、改質剤を重合体溶液中に均一に微分散させ且つ反応器から排出される反応物の滞留時間分布を狭くする事が必要となる。一方化学工業分野では反応を均一に行わしめるために工夫をこらした反応装置が種々考案されている。例えば特開昭57－170914、同57－98006に示られる反応装置は混合すべき液体が高粘度液体状態では有効であるが気液反応系では気体成分の分散が不十分で効果は期待できない。また、特開昭57－125202で提案されている連続塊状重合反応装置は仕切整流板を撹拌軸と共に回転させるため、整流板と反応容器壁との間に隙間を持たねばならない構造となっており、気－液反応系に用いると該隙間から気泡のショートパスが起こるため気泡を微分散させる事ができない。

本発明の目的は改質剤を含む液体を重合体溶液中に均一に微分散させ反応液の滞留時間分布を狭くさせ、従って均一で高い反応率を達成させうる気－液又は液－液反応装置を提供することにある。

Encl. 1 (p. 3/8)

United States Patent [19]

Mobley

[11] Patent Number: 4,578,449

[45] Date of Patent: * Mar. 25, 1986

[54] TWO-STAGE PROCESS FOR PREPARATION OF POLYPHENYLENE OXIDES

[75] Inventor: David P. Mobley, Schenectady, N.Y.

[73] Assignee: General Electric Company, Schenectady, N.Y.

[*] Notice: The portion of the term of this patent subsequent to Oct. 16, 2001 has been disclaimed.

[21] Appl. No.: 705,812

[22] Filed: Feb. 26, 1985

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 659,045, Oct. 9, 1984, abandoned, which is a continuation-in-part of Ser. No. 478,866, Mar. 25, 1983, Pat. No. 4,477,649, and Ser. No. 608,075, May 10, 1984, abandoned.

[51] Int. Cl.⁴ C08G 65/44

[52] U.S. Cl. 528/212; 526/65; 526/66; 526/67; 528/214; 528/215; 528/216; 528/217; 528/218

[58] Field of Search 528/212, 214, 215, 216, 528/217, 218; 526/65–67

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Primary Examiner—Lester L. Lee

Attorney, Agent, or Firm—William H. Pittman; James C. Davis, Jr.; James Magee, Jr.

[57] ABSTRACT

Polyphenylene oxides are prepared by the catalytic reaction of oxygen with a monohydroxyaromatic compound such as 2,6-xylenol in a solvent for reactants and product, in a two-stage process. The first stage is effected continuously in at least one and preferably not more than two back-mixed (e.g., tank) reactors, and the second stage in one or more batch reactors or, preferably, in a reaction system with limited back-mixing, typically a cylindrical reactor containing multiple agitated zones. In the case of a copper catalyst system, it is also preferred to pre-mix the non-gaseous constituents of the reaction mixture in an inert atmosphere.

24 Claims, 3 Drawing Figures

PATENT ABSTRACTS OF JAPAN

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(51)Int.Cl.	B01J 19/00

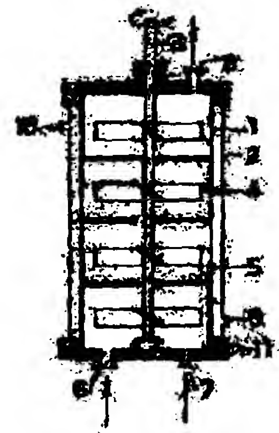
(21)Application number :	58-070071	(71)Applicant :	JAPAN SYNTHETIC RUBBER CO LTD
(22)Date of filing :	22.04.1983	(72)Inventor :	YAMAZAKI SADAHIDE OOSHIMA NOBORU TAKEUCHI MIKIO

(54) REACTION APPARATUS

(57)Abstract:

PURPOSE: To achieve uniform and high reaction ratio, by dividing a reaction vessel into a plurality of cells by stationary type dispersing plates which are provided to the inner wall of said reaction vessel and have partitioning effect.

CONSTITUTION: A reaction vessel 1 is equipped with a jacket and can be heated or cooled according to necessity and divided into four cells by stationary type dispersing plates 5 which are provided to the inner wall of said vessel 1 and have partitioning effect. Each dispersing plate 5 has an opening part formed around a stirring shaft so as to surround said shaft 3 so as to leave a gap therefrom. Each stirring blade is rotated in a direction so as to make liquid flow opposite to the entire flow direction of the liquid in the reaction vessel 1 by rotating the blade.



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Encl 3. (P. 2/2)

PATENT ABSTRACTS OF JAPAN

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(11)Publication number : 01-108972
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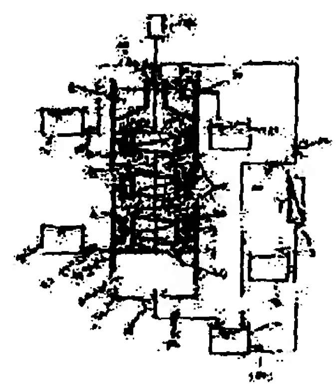
(51)Int.CI. C12M 1/00

(21)Application number : 62-265855
(22)Date of filing : 21.10.1987

(71)Applicant : SEITAI KINOU RIYOU KAGAKUHIN SHINSEIZOU GIJUTSU KENKYU KUMIAI
(72)Inventor : SAKATA MASARU
WADA HIDETOSHI

(54) REACTOR FOR LIQUID-LIQUID DIFFERENT PHASES

(57)Abstract:
PURPOSE: To improve efficiency of reaction, by providing partition plates of a structure in which a light liquid phase and heavy liquid phase are moved at suitable speeds in the reactor and carrying out continuous series multistage reaction in one vessel of the reactor.



CONSTITUTION: For example, the interior of a vessel 1 is divided into two or more compartments 3, 4 and 5 with partition plates 27 and 27 having many holes and the interiors of the respective compartments 3, 4 and 5 are divided into the interior and exterior with intermediate walls 8 to provide stirrers in the interiors in a reaction vessel for carrying out reaction in a light liquid phase and heavy liquid phase, such as hydrolysis of oils and fats with lipase, synthesis of oils and fats and various esterification reactions. An introduction port 27 for the heavy liquid phase and an overflow port 29 for the light liquid phase are provided in the upper part of the compartment 5 in the topmost layer. An introduction port 9 for the light liquid phase and outlet 30 for the heavy liquid phase are provided under the compartment 3 in the lowermost layer.

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[Translation Japanese ➔ English of JP 01-108972A]

(19) Japanese Patent Office (JP) (11) Patent Appl. Publ. Number
(12) Patent Gazette (A) 01-108972

(51) Int. Cl.⁴ ID Number Internal Ser. No. (43) Date of Publication: Apr. 26, 1989
C12M 1/00 D-8717-4B
Request for Examination: not yet filed Number of Inventions: 1 (7 pages in total)

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(54) Title of the Invention: Liquid/Liquid Hetero-Phase Reaction Apparatus

(21) Appl. Number: 62-265855
(22) Appl. Date: Oct. 21, 1987

(72) Inventor: Masaru SAKADA Nishihama 1130, Wakayama-shi, Wakayama-ken
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Specification

1. Title of the Invention

Liquid/Liquid Hetero-Phase Reaction Apparatus

2. Patent Claim

1. A liquid/liquid hetero-phase reaction apparatus for two liquid phases with different relative density that are insoluble or difficult to dissolve in one another, which is vertically partitioned into at least two compartments by partition plates having holes, wherein the compartments are provided with a middle wall partitioning them into inside and outside, wherein an agitator is attached to the inner compartment portion, wherein the uppermost compartment is provided at its upper portion with a heavy liquid face introduction port and a light liquid phase overflow port, wherein the lowermost compartment is provided with a light liquid phase introduction port below the agitator, and wherein the lowermost compartment is provided with a heavy liquid phase outlet port.

3. Detailed Description of the Invention

[Field of Application in the Industry]

The present invention relates to reaction apparatuses, in which, in liquid/liquid hetero-phase reaction systems, a continuous multi-stage reaction is carried out while stirring and mixing the hetero-phases, and moreover, the hetero-phases are continuously separated in the same reaction vessel during the reaction, and the reaction product is obtained with high efficiency.

[Prior Art Technology and Problems Thereof]

In the chemical industry, chemical reactions are for the most part hetero-phase (gas/liquid, gas/solid, liquid/solid, liquid/liquid, solid/solid) reactions, and in liquid/liquid hetero-phase reactions, which are one type of these, a large number of advantageous reactions are included. Examples of these are the hydrolysis of oils with lipase, the modification of oils, the synthesis of oils and synthesis reactions of various esters, the various peptide synthesis reactions that can be seen for example in the synthesis of the artificial sweetener aspartame using protease, or nitration reactions of organic compounds, sulfonation reactions and alkylation reactions. These hetero-phase reactions are generally performed by batch processing, in which the reaction is carried out as a fine emulsion in order to increase the reaction efficiency, and after a predetermined reaction rate has been reached, the reaction is stopped, and then the reaction products are recovered by separation into the respective phases. Furthermore, it is also possible to continuously supply the ingredients and to carry out a continuous reaction, but in this case a step of separating the emulsion becomes necessary in addition to the reaction vessel.

Thus, in reactions with liquid/liquid hetero-phase dispersion systems that cannot be dissolved into one another, it is necessary to separate the reaction system after the reaction back into the individual phases, and common examples of methods for this are stationary separation, centrifugation, or separation methods involving membranes, but when these separation steps are combined after the reaction, then the separation becomes complicated system-wise and moreover expensive, making industrial use problematic.

The inventors of this invention have already proposed a continuous reaction method with which the separation of the reaction products can be performed simultaneously while sustaining a high reaction rate in an enzymatic or microbial liquid/liquid hetero-phase reaction system (see Patent Application No. 61-122994). However, most chemical and biochemical reactions are reactions whose reaction speed decreases as the reaction rate increases, and the reaction speed can be expressed as a decay function of the reaction rate. In such reactions, in particular when continuously reacting while sustaining a high reaction rate, a tubular reaction vessel is more effective than a complete blending-type reaction vessel. That is to say, also in Patent Application No. 61-122994, in order to sustain a high reaction rate, the reaction speed becomes slow, so that a long residence time is required, and a large reaction volume becomes necessary in order to ensure the production speed. Furthermore, with complete blending-type reaction vessels, it is possible to largely overcome the drawbacks compared to tubular reaction vessels by lining up a number of reaction vessels in a straight line to form a multi-stage system, but this requires a large number of reactors, and is therefore complicated system-wise and not preferable in practice.

[Means for Solving the Problems]

In order to solve the above-described problems, the inventors have performed research with the goal of developing a reaction vessel in which a reaction can be carried out with high efficiency without loosing the features of the reaction method in Patent Application No. 61-122994, i.e. the feature of carrying out the separation of the two phases simultaneously with the reaction, and that is moreover based on the characteristics due to the different types of reaction vessels as explained above. As a result, an efficient reaction vessel was developed, in which a continuous serial multi-stage reaction can be performed in one reaction vessel by providing it with partition plates having such a structure that a light liquid phase and a heavy liquid phase are vertically movable within the reaction vessel at a suitable speed.

That is to say, the present invention provides a liquid/liquid hetero-phase reaction apparatus for two liquid phases with different relative density that are insoluble or difficult to dissolve in one another, which is vertically partitioned into at least two compartments by partition plates having holes, wherein the compartments are provided with a middle wall partitioning them into inside and outside, wherein an agitator is attached to the inner compartment portion, wherein the uppermost compartment is provided at its upper portion with a heavy liquid face introduction port and a light liquid phase overflow port, wherein the lowermost compartment is provided with a light liquid phase introduction port below the agitator, and wherein the lowermost compartment is provided with a heavy liquid phase outlet port.

The present invention provides a device, in which a continuous serial multi-stage reaction can be performed by partitioning the reaction vessel into stages with partition plates having such a structure that the light liquid phase and the heavy liquid phase are vertically movable within the reaction vessel at a suitable speed, in a reaction vessel, in which the light liquid phase and the heavy liquid phase serving as the reaction ingredients, or the reaction ingredients present in the light liquid phase and/or the heavy liquid phase are converted into the reaction products, and the reaction products present in the light liquid phase and/or the heavy liquid phase of the non-blended portion can be retrieved, by blending the light liquid phase and the heavy liquid phase near their interface while leaving portions of the light liquid phase and the heavy liquid phase that do not blend in the reaction vessel, in which the light liquid phase and the heavy liquid phase exist separated into two vertical layers.

Consequently, with the present invention, a more compact reaction vessel can be realized for a two-phase hetero-phase reaction, and moreover a superior reaction method can be established, in which the separation of the two phases can be carried out simultaneously with the reaction.

A preferable embodiment of the present invention is explained in

more detail with reference to the drawings, taking as an example a liquid/liquid two-phase reaction between an aqueous solution as the heavy liquid phase and a non-aqueous solution phase with a specific gravity that is smaller than water as the light liquid phase. As the reaction example, a liquid/liquid two-phase reaction expressed by A + B ➔ C + D (wherein A and B are the reaction ingredients, and C and D are the reaction products. A and C are water-soluble, and B and D are non-water-soluble) is explained with reference to Fig. 1. Fig. 1 shows an example of a reaction vessel having the features of the present invention. From the bottom of the reaction vessel 1, 2 is an aqueous phase, and 3, 4 and 5 are reaction portions, partitioning the reaction vessel 1 into three compartments with partition plates 27. If the number of compartments is large, then the efficiency improves, but the device also becomes complicated and expensive. Consequently, 2 to 10 compartments are preferable. In order to form a fine emulsion of the non-aqueous solution phase and the aqueous phase and react them efficiently, the two phases are blended by helical screw-type agitator blades 25 having a draft tube 8 in the portions that are partitioned by partition plates. 6 is the non-aqueous solution (light liquid) phase. As shown in Fig. 1, when the uppermost portion and the lowermost portion of the reaction vessel are respectively provided with baffle plates 10 and 22, then complete mixing of the liquid at the uppermost portion and the lowermost portion of the reaction vessel can be prevented, and a portion at which the non-aqueous solution phase and the aqueous phase are in a separated state can be formed, which is preferable.

The reaction ingredient A (aqueous phase) and the reaction ingredient B (non-aqueous solution phase) are fed with pumps 19 and 18 at a constant ratio from a reaction ingredient (aqueous phase) storage tank 16 and a reaction ingredient (non-aqueous solution phase) storage tank 17 through an aqueous (heavy phase) introduction port 28 and a non-aqueous solution (light phase) introduction port 9 into the reaction vessel. The aqueous and the non-aqueous solution can be fed in as concurrent flows or as countercurrent flows, but ordinarily it is preferable that they are fed in as countercurrent flows.

For the partition plates partitioning the inside of the reaction vessel, partition plates are used with which the blending of the liquids at the upper portion and the lower portion, with the partition plates as the borders, is as low as possible, and when a non-aqueous solution and water are supplied continuously, their traveling speeds are compatible with those supply speeds. That is to say, most preferable are partition plates, with which the liquid phases move vertically at just the supply speed of the non-aqueous solution and the water. There is no particular limitation regarding the shape and the material of the partition plates, as long as the above-described conditions are met, and plates with the shape of, for example, bubble trays, bubble-cap trays or perforated trays used for tray towers for distillation or extraction or the

like can be used. For the material, stainless steel, glass, ceramics or synthetic resins or the like can be used.

The uppermost compartment is provided with an overflow port 29 for the non-aqueous solution (light liquid phase), and the lowermost compartment is provided with a water (heavy liquid phase) outlet port 30, and the production materials D and C are retrieved from these outlet ports.

Using the method of the present invention, the separation of the production materials can be performed simultaneously with the reaction, so that batch operation is, of course, possible, but also continuous reactions or semi-continuous reactions in which the reaction ingredients are supplied while continuously extracting the production materials can be performed. Furthermore, by partitioning the inside of the reaction vessel into several stages with partition plates and preventing the complete blending of the liquids, an efficient reaction can be performed, the reaction time can be shortened, the reaction vessel can be made smaller, and the concentration of the reaction products can be increased, for example.

If a draft tube 8 serving as the middle wall and mixing blades 25 as shown in Fig. 1 are used, then there is no particular limitation regarding the diameter of the draft tube, and the diameter can be decided in accordance with the reaction to be performed, but it is preferable that the diameter is 5 to 90% of the diameter of the reaction tank. The rotation speed of the agitator blades should be set such that the lower layer in the reaction vessel is stirred up well, the non-aqueous solution phase and the aqueous phase blend near their interface, and moreover portions remain at the top and the bottom of the reaction vessel where the non-aqueous solution phase and the aqueous phase are not mixed.

As shown in Fig. 1, it is also possible to use a filler 7. In that case, there is no particular limitation to the form of the filler, and it is possible to fill, for example, with fillers such as Raschig rings, Lessing rings, Berl saddles, Intalox saddles, and pall rings, which are used generally and ordinarily as fillers, or with cylindrically shaped nets. There is no particular limitation to the material, and fillers made of metal, porcelain and plastic can be used, for example.

Using a filler increases the contact efficiency between the aqueous phase and the non-aqueous solution phase, and in systems using a catalyst or a biocatalyst such as enzymes or microorganisms, the contact efficiency between the catalysts and the reaction ingredients is improved, and an efficient reaction can be performed. However, if these conditions are met even without using a filler, then it is not necessary to use a filler.

If the reaction is performed using this reaction vessel and with an ordinary chemical catalyst or a biocatalyst such as enzymes or microorganisms, then the catalysts used for the reaction may be

maintained within the reaction vessel with high efficiency, but they are sometimes dissolved somewhat in the aqueous phase or the non-aqueous solution phase. Consequently, considering the efficient use of the catalysts and their influence on the quality of the production materials, it is preferable to carry out concentration and recovery of the catalysts.

It should be noted that in the present invention, "catalysts" means not only ordinary chemical catalysts, but all catalysts, including biocatalysts such as enzymes and microorganisms.

Examples for the efficient concentration and recovery of catalysts include methods such as stationary separation, centrifugation and membrane separation, but for continuous separation, it is preferable to use an ultrafiltration membrane. Regarding the ultrafiltration membrane to be used, there is no particular limitation regarding material and shape, as long as the catalyst used for the reaction cannot pass through it. To recover catalyst dissolved in the aqueous phase, it is preferable to use a hydrophilic material, such as a cellulose acetate membrane, a polyacrylonitrile membrane, a polysulphone membrane, or a polyamide membrane. To recover catalyst dissolved in the non-aqueous solution phase, it is preferable to use a hydrophobic material, such as a polypropylene membrane, a polyethylene membrane, or a Teflon membrane. Furthermore, membranes of inorganic materials such as porous glass or porous ceramics can be used preferably for membrane separation of either the aqueous phase or the non-aqueous solution phase. As for shape, it is possible to use any kind of shape, such as flat, tube-shaped, spiral-shaped or hollow fiber membranes. The molecular weight cut-off of the ultrafiltration membrane depends on the catalyst used for the reaction, and the membrane should have a pore diameter that impedes the passing of the catalyst. There is no particular limitation, but in general, about 3000 to 50000 is preferable. Aqueous phase or non-aqueous solution phase not including the catalyst should be extracted continuously by ultrafiltration, and concentrate of the catalyst should be returned continuously or semi-continuously to the reaction system.

It should be noted that if almost all of the catalyst is kept inside the reaction vessel, and the dissolution into the aqueous phase or the non-aqueous solution phase can be ignored, then the separation of the catalyst by ultrafiltration is not necessary. It is further possible to fill in a catalyst that is affixed to an insoluble carrier by various methods beforehand, and also in this case, a catalyst recovery step by ultrafiltration is not necessary. Or, it is also possible to omit the ultrafiltration step, and to add fresh catalyst in correspondence with the catalyst portion that has been dissolved in the aqueous phase or the non-aqueous solution phase.

When such a method is used, then without carrying out special pre-processing, the catalyst can be kept inside the reactor vessel and

can be recovered and recycled with high efficiency. And without carrying out special pre-processing, the catalyst can be retained in the filler by adsorption or the like, or a catalyst previously subjected to an insolubility treatment by various methods (carrier catalyst, immobilized biocatalyst, etc.) is used, or no filling material is used and the catalyst is used in free form. The method to be used should be selected in accordance with the characteristics of the catalyst and the reaction conditions, etc.

Features of the present invention are that in a reaction vessel in which a reaction is carried out while blending two upper and lower layers at their interfaces inside the reaction vessel, the reaction is carried out while leaving portions where no blending occurs at an upper layer portion and a lower layer portion in the reaction vessel, the light liquid phase and the heavy liquid phase can be retrieved independently and simultaneously to the reaction, the reaction vessel is provided with partition plates that prevent complete mixing of the liquids in the reaction vessel and that have a structure such that the light liquid phase and the heavy liquid phase can travel at the same speed as their respective supply speeds, so that an efficient reaction, that is, a continuous serial multi-stage reaction can be performed in one reaction vessel. Consequently, the production materials can be obtained simultaneously while continuously adding reaction ingredients. Furthermore, since the reaction is carried out continuously, the concentration of the various production materials in the reaction vessel can be held constant.

The method of the present invention can be applied to various reactions in liquid/liquid hetero-phase systems of a light phase and a heavy phase, such as the afore-mentioned hydrolysis reactions of oils by lipase, synthesis of triglycerol with lipase, ester exchange reactions of triglyceride, or peptide synthesis reactions with protease such as the synthesis of the artificial sweetener aspartame (aspartylphenylalanine methylester) from carbobenzyloxy-1-aspartic acid and γ-phenylalanine methylester with thermolysin, and in addition to such biochemical reactions, the present invention is also widely applicable to reactions in liquid/liquid two-phase systems, such as nitration reactions, sulfonation reactions or alkylation reactions of organic compounds, but there is no particular limitation to these.

[Working Examples]

The following is an explanation of working examples of the present invention, however the present invention is not limited to these working examples.

Working Example 1

The hydrolysis of oils with enzymes using the method of the present invention is explained. In this case, the reaction materials are

oil and water, the enzyme is lipase, and the reaction products are fatty acids and glycerin. The inventors have already found that in the course of the hydrolysis of oils using lipase, the reaction product glycerin contributes greatly to the stability of the lipase. According to research performed by the inventors, when the glycerin concentration in the aqueous phase of the reaction system is in the range of 10 to 40 wt%, then the enzyme is stabilized and the oil hydrolysis proceeds favorably. With the method of the present invention, the concentration of the various components can be easily held constant in the various stages of the reaction vessel partitioned by the partition plates and consequently, it can be applied favorably to the hydrolysis of oil with lipase. That is to say, by suitably adjusting the supply rates of oil and aqueous phase, the glycerin concentration in the aqueous phase can be controlled while sustaining a high oil break-down rate.

Fig. 1 shows an example of a preferable working system in accordance to the present invention. First, the hydrolysis of soybean oil by lipase was carried out with the reaction system shown in Fig. 1. In this hydrolysis of oils with lipase, numeral 9 in Fig. 1 is an oil supply nozzle, 11 is a fatty acid solution storage tank, 14 is a storage tank for glycerine aqueous solution membrane treatment, 15 is a glycerin water storage tank, 16 is a water storage tank, and 17 is an oil storage tank.

1 kg of broken down fatty acid (with fatty acid content of 85%) obtained by enzymatically breaking down soybean oil, 1 kg of 15 wt% glycerin water and 2g lipase (320000 units/g) from Candida cylindracea were given into the reaction tank 1, and the reaction was performed while keeping the reaction tank at 30°C. The ratio of the diameter of the reaction tank to the diameter of the draft tube 8 is 10 : 6. For the agitator blades, ribbon blades 25 as shown in Fig. 1 were used, and the stirring was performed at a circumferential speed of about 0.5 m/sec. The soybean oil (with fatty acid content of 0%) was continuously supplied from the oil storage tank 17 into the reaction tank 1 through the nozzle 9 at the bottom of the reaction tank 1 with a pump 18 at a flow rate of 50 g/hr. 15 wt% glycerin water, which has previously been put into the water storage tank 16, is continuously supplied from the top of the reaction vessel with a pump 19 at a flow rate of 50 g/hr. That is to say, the oil phase and the aqueous phase were supplied into the reaction vessel such that their average residence time in the reaction tank is 20 hours. A hydrolysis reaction with high efficiency is performed without complete mixing, due to the partitioning of the reaction tank into three stages with partition plates. Furthermore, by providing baffle plates 10 and 22 at the top and the bottom of the reaction tank, on the upper side 6 or lower side 2 thereof, fatty acid including almost no water or glycerin water including almost no oil is obtained. Thus, an amount of fatty acid corresponding to the supplied soybean oil continuously overflowed and was retrieved from the overflow port 29 of the light liquid phase, glycerin water was continuously

extracted with a pump 20 from the outlet port 30 at the bottom of the reaction tank, and after it has been temporarily stored in the storage tank 14, the enzyme dissolved in the aqueous phase was concentrated and recovered by an ultrafiltration membrane 13, and the reaction was carried out while making adjustments such that the extraction amount of glycerin water was 50 g/hr. In this working example, a polyacrylonitril membrane (with a molecular weight cut-off of 30000) was used for the ultrafiltration membrane, and the enzyme was concentrated semi-continuously and returned to the reaction tank.

Using such a reaction apparatus, the reaction was continued while continuously supplying soybean oil and glycerin water solution and while continuously retrieving fatty acid solution and glycerin water solution.

After 20 hours, (equal to the average residence time in the reaction tank), the reaction liquid was collected from the portions 3, 4 and 5 of the reaction tank 1, the acid value and the saponification value of those various oil phases was measured, and the glycerin concentration of the aqueous phases was measured. In portion 3, an acid value of 155 and a saponification value of 198, in portion 4, an acid value of 181 and a saponification value of 199, and in portion 5, an acid value of 190 and a saponification value of 200 were measured. When the rate of hydrolysis was calculated by the equation below, rates of hydrolysis of 78%, 91% and 95% were determined for the portions 3, 4 and 5.

rate of hydrolysis of oil (%) = (acid value / saponification value) × 100

Furthermore, the glycerin concentrations at the portions 3, 4 and 5 were 24%, 16.4 and 15.4%. It should be noted that the breakdown rate of the portion 5 is equal to the breakdown rate of the fatty acid solution obtained in the fatty acid solution storage tank 11, and the glycerin concentration in the aqueous phase in the portion 3 is equal to the glycerin concentration of the glycerin water solution in the glycerin water solution storage tank 15.

Similarly, Table 1 shows the breakdown rates and the glycerin concentrations that were measured at those portions of the reaction tank after 40 hours, after 60 hours, after 80 hours and after 100 hours after beginning to supply the soybean oil.

Table 1

reaction time (hr)		20	40	60	80	100
oil breakdown rate (%)	portion 3	78	77	77	77	76
	portion 4	91	89	89	88	89

	portion 5	95	93	93	92	93
glycerin concentr. (%)	portion 3	24.0	23.6	23.1	24.0	23.0
	portion 4	16.4	16.4	16.0	15.8	16.2
	portion 5	15.4	15.3	15.4	15.4	15.3

Thus, even when a continuous reaction of 100 hours is performed, the enzyme loses none of its activity, a soybean oil breakdown ratio of 92 to 95% is attained, and the glycerin concentration in the aqueous phase can be sustained at 23 to 24%.

On the other hand, the water component in the fatty acid solution obtained in the fatty acid solution storage tank 11 was less than 0.5%. Also the glycerin water that has passed through the ultrafiltration membrane yielded glycerin water of high quality. Thus, it was found that by using this reaction system, the reaction and the separation of the reaction products could be performed simultaneously, while the enzyme could be recovered and recycled with high efficiency, and a high breakdown ratio could be attained.

Comparative Example 1

The continuous hydrolysis of soybean oil was performed using a reaction tank not having partition plates that partition the reaction tank into several stages, as used in the reaction tank in Working Example 1.

1 kg of broken down fatty acid (with fatty acid content of 85%) obtained by enzymatically breaking down soybean oil, 1 kg of 20 wt% glycerin water and 2g lipase (320000 units/g) from Candida cylindracea were given into the reaction tank, and the reaction was performed while keeping the reaction tank at 30°C. The ratio of the diameter of the reaction tank to the diameter of the draft tube 8 is 10 : 6. For the agitator blades, ribbon blades were used, and the stirring was performed at a circumferential speed of 0.5 m/sec.

The soybean oil was supplied from the bottom of the reaction tank at a flow rate of 50 g/hr and water was supplied from the top at a flow rate of 25 g/hr, and a continuous reaction was carried out. That is to say, they were supplied to the reaction tank such that the average residence time of the soybean oil in the reaction tank is 20 hours, and the glycerin concentration in the aqueous phase can be kept at about 20%.

Thus, the fatty acids produced in the same manner as in Working Example 1 were continuously retrieved by overflowing, and sweet water was continuously retrieved from the system after recovering the enzyme dissolved in the aqueous phase with the ultrafiltration membrane.

Table 2 shows the hydrolysis rates of the soybean oil and the glycerin concentrations that were measured at various reaction times.

Table 2

reaction time (hr)	20	40	60	80	100
oil breakdown rate (%)	86	85	86	85	85
glycerin concentration (%)	20	19	18	19	19

Thus, it can be seen that even when continuously reacting for 100 hours, a loss of enzyme activation cannot be observed, but the breakdown rate of the soybean oil is 85 to 86%, which is much lower than in Working Example 1.

Working Example 2

Using the same apparatus as in Working Example 1, the amounts of the initially inserted broken down soybean solution, the 15 wt% glycerin water solution and the enzyme were the same as in Working Example 1, the soybean supply amount was set to the same 50 g/hr as in Working Example 1, but the supply amount of the 15 wt% glycerine water solution was changed to 25 g/hr. That is to say, the average residence time of the aqueous phase was set to 40 hours. Thus, continuous hydrolysis of the soybean oil was performed. Table 3 shows the oil breakdown rate and the glycerin concentration at the various portions of the reaction tank after the various reaction times.

Table 3

reaction time (hr)		20	40	60
oil breakdown rate (%)	portion 3	60	61	59
	portion 4	85	84	95
	portion 5	91	92	91
glycerin concentr. (%)	portion 3	33.2	35.2	35.3
	portion 4	18.0	18.6	18.3
	portion 5	15.7	15.7	15.5

Thus, it was found that by adjusting the supply speed of the aqueous phase, a high breakdown rate could be maintained and moreover a high glycerin water concentration could be attained.

4. Brief Description of the Drawings

Fig. 1 is a diagram showing one example of a reaction apparatus according to the present invention.

1 ... reaction tank
2 ... heavy liquid phase portion
3 to 5 ... reaction portions
6 ... light liquid phase portion
7 ... filler
8 ... draft tube
9 ... reaction ingredient (light liquid phase) introduction port
10 ... upper baffle plate
11 ... reaction product (light liquid phase) storage tank
12 ... dam
13 ... ultrafiltration membrane
14 ... storage tank for reaction product (heavy liquid phase) membrane treatment
15 ... reaction product (heavy liquid phase) storage tank
16 ... reaction ingredient (heavy liquid phase) storage tank
17 ... reaction ingredient (light liquid phase) storage tank
18 to 21 ... pumps
22 ... lower baffle plate
23 to 24 ... valves
25 ... agitator blades
26 ... agitator motor
27 ... partition plates in reaction tank
28 ... heavy liquid phase introduction port
29 ... reaction product (light liquid phase) overflow port

30 ... reaction product (heavy liquid phase) outlet port

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